

A Proposal for a Modified Møller-Plesset Perturbation Theory

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Abstract

A modified version of the Møller-Plesset approach for obtaining the correlation energy associated to a Hartree-Fock ground state is proposed. The method is tested in a model of interacting fermions that allows for an exact solution. Using up to third order terms improved results are obtained, even in the limit of loosely bound particles.

The study of molecules and larger systems is seriously constrained by their many body nature. Several approximation schemes have been devised over the years, among which the Hartree-Fock (HF) method is one of the oldest and most fruitful. Because it treats interactions in a mean field way particle correlations are left out, however, a shortcoming that can limit severely the validity of its results. One may improve over HF by treating correlations as a perturbation. In the so-called Møller-Plesset method, a Rayleigh-Schrödinger perturbative expansion that is naturally suggested by the same structure of the HF solution[1,2,3,4] is adopted. This formalism reduces the correlation energy to an infinite series in the perturbation, of which only the first few terms need to be computed in practice. This scheme has been used for a long time as a good starting point to study correlation effects in molecular systems. However, this method is useful only if the perturbation series is rapidly convergent, which is not always true[5]. Failures of the Møller-Plesset method have been documented even for small molecules [5,6,7]. In this paper we present a

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variation of the Møller-Plesset approach that appears to give accurate results in low order perturbation schemes even when particles are loosely bound, such as in chemical bonds.

Consider the many-particles Hamiltonian

$$\mathcal{H} = \sum_i h(i) + \sum_{i,j>i} v(i,j), \quad (1)$$

where $h(i) = h(\mathbf{r}_i)$ is the sum of the one-particle kinetic energy plus external potential energy, and $v(i,j) = v(\mathbf{r}_i, \mathbf{r}_j)$ is the two-particles interaction energy. The HF approximation to the ground state of a system of identical fermions leads to a variational wave function Φ in the form of a Slater determinant, constructed with one-particle orbitals that satisfy the equations

$$\left[h(i) + \sum_b (\mathcal{F}_b(i) - \mathcal{K}_b(i)) \right] \phi_n(i) = \epsilon_n \phi_n(i), \quad (2)$$

where \mathcal{F}_b and \mathcal{K}_b are the Coulomb and exchange operators, respectively. Here and in what follows summation over indices a, b, c run over all occupied states, while n runs over all possible states. The eigenvalues satisfy the relation

$$\epsilon_n = \langle n|h|n \rangle + \sum_b \langle nb||nb \rangle, \quad (3)$$

where

$$\langle mn||mn \rangle = \langle mn|mn \rangle - \langle mn|nm \rangle, \quad (4)$$

$$\langle mn|pq \rangle = \int \phi_m(1)^* \phi_n(2)^* v(1,2) \phi_p(1) \phi_q(2) d1d2. \quad (5)$$

In the above expression 1 and 2 represent the one-electron variables of coordinate and spin. The energy of the HF state is

$$\begin{aligned} E_{HF} &= \sum_a \langle a|h|a \rangle + \frac{1}{2} \sum_{a,b} \langle ab||ab \rangle \\ &= \sum_a \epsilon_a - \frac{1}{2} \sum_{a,b} \langle ab||ab \rangle, \end{aligned} \quad (6)$$

where to obtain (6) we have used Eq. (3). The operator

$$\mathcal{H}_{HF} = \sum_n \epsilon_n \hat{c}_n^\dagger \hat{c}_n - \frac{1}{2} \sum_{a,b} \langle ab||ab \rangle \hat{c}_a^\dagger \hat{c}_b^\dagger \hat{c}_b \hat{c}_a \quad (7)$$

is then a natural choice for an effective HF hamiltonian, diagonal in the HF orbitals and having as ground state the HF energy E_{HF} . In Eq. (7) \hat{c}_n^\dagger (\hat{c}_n) is the creation (annihilation) operator of a particle in the state ϕ_n . This hamiltonian

operator is the starting point to construct a perturbation expansion for the correlation energy using as perturbation $V_{HF} = \mathcal{H} - \mathcal{H}_{HF}$ [4].

A second choice for a hamiltonian is also possible, however. Equation (6) may be written in the form,

$$E_{HF} = \sum_a (\epsilon_a - \frac{1}{2} \sum_b \langle ab || ab \rangle), \quad (8)$$

suggesting as an alternate hamiltonian

$$\mathcal{H}_{MHF} = \sum_n (\epsilon_n - \frac{1}{2} \sum_b \langle nb || nb \rangle) \hat{c}_n^\dagger \hat{c}_n, \quad (9)$$

also diagonal in the HF orbitals. The correlation energy can again be described in terms of a perturbation, this time of the form $V_{MHF} = \mathcal{H} - \mathcal{H}_{MHF}$. Note that while Eq. (7) involves an overall constant, Eq. (9) subtracts from each single particle energy a different correction. Although both forms yield the same ground state energy, the energy of excited states are different, affecting the various orders contributions in a perturbation expansion. For instance, the second order correction to the HF ground state energy has the form[4]

$$E^{(2)} = \sum_{\Phi'} \frac{|\langle \Phi | \mathcal{H} | \Phi' \rangle|^2}{E_{HF} - E_{\Phi'}} = \frac{1}{4} \sum_{abrs} \frac{|\langle ab || rs \rangle|^2}{E_{HF} - E_{\Phi'}}, \quad (10)$$

where in the numerator we have used the fact that the excited state Φ' is orthogonal to the ground state. This is the first finite correction in the Rayleigh-Schrödinger perturbation expansion since for either choice of hamiltonian the first order term vanishes. Only doubly excited states $\Phi' = \Phi_{ab}^{rs}$ (ϕ_a replaced by ϕ_r and ϕ_b replaced by ϕ_s in the Slater determinant Φ , with ϵ_r, ϵ_s above the Fermi energy) contribute[4]. The choice of hamiltonian affects the excitation energies in the denominator, which have the form

$$E_{HF} - E_{\Phi_{ab}^{rs}} = \begin{cases} \epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s, & \mathcal{H}_0 = \mathcal{H}_{HF} \\ \tilde{\epsilon}_a + \tilde{\epsilon}_b - \tilde{\epsilon}_r - \tilde{\epsilon}_s, & \mathcal{H}_0 = \mathcal{H}_{MHF} \end{cases}, \quad (11)$$

where $\tilde{\epsilon}_n = \epsilon_n - \frac{1}{2} \sum_b \langle nb || nb \rangle = \frac{1}{2}(\epsilon_n + \langle n | h | n \rangle)$. Replacing in Eq. (10) both forms clearly lead to different results. A similar analysis of the third and higher order terms in the perturbation expansion yields again different results. For example, in the third order correction, besides the change of denominators in the standard Möller-Plesset expression[4], an additional term $\Delta E^{(3)}$ appears, which can be cast in the compact form, useful in computations,

$$\Delta E^{(3)} = -E^{(2)} - \frac{1}{4} \sum_{abrs} \frac{(h_{rr} + h_{ss} - h_{aa} - h_{bb}) |\langle ab || rs \rangle|^2}{(\tilde{\epsilon}_r + \tilde{\epsilon}_s - \tilde{\epsilon}_a - \tilde{\epsilon}_b)^2}, \quad (12)$$

where $h_{nn} = \langle n|h|n \rangle$. The first element of Eq. (12) cancels the second order energy correction. However, the second element of Eq. (12) is also second order in the interaction. Replacing Eqs. (10) and (11) in (12) and performing simple operations $\Delta E^{(3)}$ can be put in a form that reveals explicitly the third order character of the correction.

Table 1

Ground state energies of a system of two harmonically confined spin 1/2 particles interacting through a harmonic potential of strength k . Several approximations are included: Hartree-Fock (HF), Møller-Plesset perturbation theory of orders $n = 2, 3$ (MP n), modified MP n (MMP n), as well as the exact values. Repulsive interactions are represented by negative values of the elastic constant k .

| k | HF | MP2 | MP3 | MMP2 | MMP3 | Exact |
|-------|-------|-------|-------|-------|-------|-------|
| -0.25 | 1.732 | 1.655 | 1.836 | 1.702 | 1.710 | 1.707 |
| -0.24 | 1.744 | 1.681 | 1.803 | 1.717 | 1.724 | 1.721 |
| -0.22 | 1.766 | 1.725 | 1.784 | 1.745 | 1.750 | 1.748 |
| -0.20 | 1.789 | 1.760 | 1.791 | 1.772 | 1.776 | 1.775 |
| -0.18 | 1.811 | 1.791 | 1.808 | 1.798 | 1.801 | 1.800 |
| -0.16 | 1.833 | 1.819 | 1.828 | 1.823 | 1.825 | 1.825 |
| -0.09 | 1.908 | 1.905 | 1.906 | 1.905 | 1.906 | 1.906 |
| -0.04 | 1.960 | 1.959 | 1.959 | 1.959 | 1.959 | 1.959 |
| -0.01 | 1.990 | 1.990 | 1.990 | 1.990 | 1.990 | 1.990 |
| 0.00 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 |
| 0.04 | 2.040 | 2.039 | 2.039 | 2.039 | 2.039 | 2.039 |
| 0.16 | 2.154 | 2.150 | 2.149 | 2.149 | 2.149 | 2.149 |
| 0.36 | 2.332 | 2.319 | 2.314 | 2.316 | 2.313 | 2.311 |
| 0.64 | 2.561 | 2.534 | 2.522 | 2.525 | 2.516 | 2.510 |
| 1.00 | 2.829 | 2.784 | 2.762 | 2.767 | 2.749 | 2.732 |

In order to assess the convenience of either formulation for obtaining corrections due to correlations we have solved a system of two spin-1/2 particles in a harmonic potential, interacting through a harmonic force. The reason for the choice is that this is an interacting system involving identical fermions that may be solved exactly[8]. The Hamiltonian is

$$H = \frac{1}{2} \left(-\Delta_1 + r_1^2 \right) + \frac{1}{2} \left(-\Delta_2 + r_2^2 \right) + \frac{1}{2} k (\mathbf{r}_1 - \mathbf{r}_2)^2, \quad (13)$$

where the coordinates and the energy are given in the oscillator units of the confinement potential. The exact ground state energy is

$$E_0 = 1 + \sqrt{1 + 2k}. \quad (14)$$

The model contains the parameter k that allows the study of attractive ($k > 0$) as well as repulsive ($k < 0$) interactions. Equation (14) shows that $k = -0.5$ is the lowest value for which a bound state exists.

We have solved the problem in two dimensions, using a basis of noninteracting harmonic oscillators eigenfunctions

$$\phi_{n_x, n_y}(x, y) = \varphi_{n_x}(x)\varphi_{n_y}(y), \quad 0 \leq n_x + n_y \leq 5, \quad (15)$$

where the $\varphi(x)$ are the usual one-dimensional harmonic oscillator eigenfunctions. The set (15) is an exact solution when $k = 0$. The HF solution is obtained by solving the self-consistent-field equation for closed shell configurations[4].

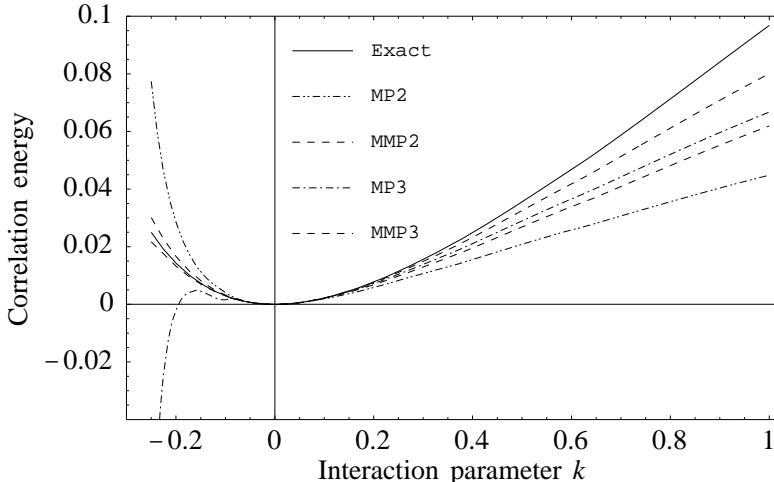


Fig. 1. Correlation energy for a system of two harmonically confined spin 1/2 particles interacting through a harmonic potential of strength k . The exact result is included, as well as corrections up to second and third order for the Møller-Plesset (MP) and modified Møller-Plesset (MMP) choices of zeroth-order hamiltonian.

Table 1 shows the ground state energy for the Hamiltonian (13) calculated using the standard Møller-Plesset perturbation theory of order $n = 2, 3$ (MP n), and our modified form, MMP n . Figure 1 shows the exact correlation energy $E_{corr} = E_{HF} - E$ for different values of k , together with results obtained for the two choices of HF hamiltonian, in second and third order of perturbation theory. Notice that MMP n yields better results throughout. Notice also that the usual MP n fails badly in both orders of approximation when the system becomes more loosely bound, as k approaches the critical value -0.5. In fact, convergence problems prevent solving the HF self-consistent equations for k beyond -0.25. By contrast, MMP n continue to be good approximations even

in this range of k . This strongly suggests that the modified perturbation theory may be more suitable in treating outer shells of bound systems, such as electrons participating in chemical bonds. Investigation of this ansatz is in progress.

A well known feature of HF theory is that the many body ground state energy is not the bare sum of energies of filled single particle orbitals. Interactions are counted twice and this overestimation is corrected for by subtracting the constant explicit in Eq. (3). The remarkable improvement obtained over the usual Møller-Plesset approach in our test example may be traced to the fact that this latter method does not correct the single particle energies for such effect. In fact, the energy denominator appearing in the perturbative corrections to all orders in such case may grossly depart from the true two-particle excitation energy that the numerator in the expression is weighting. By contrast, in the method proposed here each self energy is corrected accordingly. It is hoped that our results will stimulate the use of the proposed method in situations where corrections to the Hartree-Fock approximations may be necessary.

Support from FONDECYT grants 1020829 and 7020829, and the Third World Academy of Sciences, is gratefully acknowledged.

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